REMARKS

In the present amendment, independent claim 12 has been amended to delete the polymer light absorbent having a group represented by formula (IX), from the Markush grouping of polymer light absorbents recited in the claim. Also, the spelling of "atoms" has been corrected. In addition, claim 19 has been amended to depend solely from claim 18. Entry of the amendments is respectfully requested.

Claims 12, 14-22 and 24 are pending in the application. Of these, claims 14-18, 20, 22 and 24 have been withdrawn from consideration.

Response to Section 102(b) Anticipation Rejection over Skoultchi

Claim 12 is rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Skoultchi (3,575,925).

The Examiner asserts that the polymer compositions of Examples I, III, V and VI of Skoultchi anticipate the anti-reflective coating material composition of Applicants wherein present polymer formulas (XIII) and (VXIV) are considered. In each case, the Examiner says n=0 and m=0 in Applicants' formulas. For present formula (XIII) and Skoultchi Example VI, the Examiner says, A_1 is a substituted naphthyl group (-napthyl-C(=O)-). For present formula (XIII) and Skoultchi Example I, the Examiner says, A_1 is -phenyl-C(=O)-. For present formula XIII and Skoultchi Example III, A_1 is -phenyl-C(=O)-. For present formula VXIV and Skoultchi Example V, A_2 is -C(=O)-phenyl. For present formula (VXIV), the Examiner says, A_2 is -C(=O)-naphthyl. (Presumably, the Examiner is referring to Skoultchi Example VI in this instance).

The Examiner asserts that these polymer compositions of Skoultchi are inherently useful as anti-reflective coating materials.

Applicants submit that this rejection should be withdrawn because Skoultchi does not disclose or render obvious the bottom anti-reflective coating material composition of the present invention.

The compounds described in Skoultchi have a different structure from those of the present invention and thereby, clearly have a different function from the compounds of the present invention. The compounds of Skoultchi are photosensitive because they have a carbonyl group as a linkage group between the naphthalene ring and the aromatic ring.

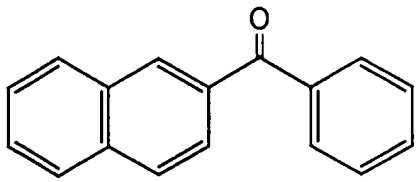
In contrast, the compounds of the present invention have a structure in which the aromatic ring is directly linked to the naphthalene ring, and do not react and do not undergo a chemical change even if exposed to light.

Thus, the compounds for use in the working examples of Skoultchi have a structure in which the aromatic ring is linked to the naphthalene ring via a carbonyl group. In contrast, the compounds of the present invention have a structure in which the aromatic ring is directly linked to the naphthalene ring. Thus, Skoultchi does not constitute a proper basis for rejecting the present claims.

The Examiner cites multiple references related to photosensitive compositions, but a photosensitive composition and a bottom anti-reflective coating material composition are different and have different properties. A photosensitive composition reacts to generate a change such as a solubilization or insolubilization upon an exposure, and then either the exposed areas or

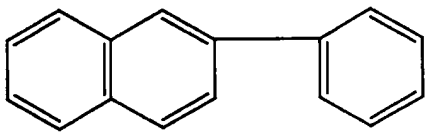
the unexposed areas are removed by development to form an image. In contrast, a bottom anti-reflective coating material composition can prevent a reflection by absorption of light, and does not essentially require a chemical change in the exposed area. In addition, the photosensitive composition and the bottom anti-reflective coating material composition are a different using mode, e.g., as shown in EP 0159428B1 (especially see the figures). A copy of EP '428 is submitted herewith. Accordingly, it can hardly be said that a composition used as a photosensitive composition is inherently useful as a bottom anti-reflective coating material composition.

The naphthyl phenyl ketone structure below which is described in the working examples of Skoultchi shows a photosensitive property:



It is known that the aromatic ketone compound as described above shows a photosensitive property. This is described in *PHOTOREACTIVE POLYMERS* (1989) by Arnost Reiser, Chapter 4, pages 113 et seq. submitted herewith. The excited triplet states of the aromatic ketone compound cause a hydrogen abstraction reaction, and therefrom, a radical polymerization reaction is initiated, and as the result, the exposed area hardens to form an image. The naphthyl phenyl ketone structure generates the excited triplet states to react and this is described as Sensitizer No. 6 in Table 1 on page 930 in Wendell L. Dilling et al, Journal of American Chemical Society, Vol. 92, No. 4 (170) submitted herewith.

In contrast, the compound of the present invention in which the aromatic ring is directly linked to the naphthalene ring, as shown,



has no carbonyl group, and does not cause a reaction such as the hydrogen abstraction.

In view of the above, Applicants submit that the § 102(b) rejection of claim 12 over Skoultchi should be reconsidered and withdrawn.

Response to Section 102(e) Anticipation Rejection over Mizutani et al

Claims 12 and 21 are rejected under 35 U.S.C. § 102(e) as allegedly being anticipated by Mizutani et al (6,090,531).

The Examiner asserts that certain polymers disclosed or suggested in Mizutani et al are within the scope of present formula (IX).

As noted above, Applicants have deleted formula (IX) from independent claim 12 in the present Amendment.

Accordingly, the Examiner is respectfully requested to reconsider and withdraw the rejection over Mizutani et al.

Response to Section 102(b) Anticipation Rejection over Teuscher

The Examiner states that claim 12 is rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Teuscher (3,943,108).

As in the case of Mizutani et al, the Examiner asserts that certain polymers disclosed or suggested in Teuscher et al are within the scope of formula (IX) of present claim 12.

As noted, Applicants have deleted formula (IX) from claim 12 in the present Amendment.

Accordingly, the Examiner is respectfully requested to reconsider and withdraw the rejection of claim 12 over Teuscher.

Response to Section 102(b) Anticipation Rejection over Unruh et al '103

Claim 12 is rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Unruh et al (2,716,103).

As in the case of Mizutani et al and Teuscher, the Examiner asserts that certain compositions disclosed or suggested in Unruh et al are within the scope of present formula (IX).

As noted, formula (IX) has been deleted in the present Amendment.

Accordingly, the Examiner is respectfully requested to reconsider and withdraw the rejection of claim 12 over Unruh et al. '103.

Response to Section 102(b) Anticipation Rejection over Unruh et al '097

Claim 12 is rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Unruh et al (2,716,097).

The Examiner asserts that Unruh et al '097 discloses or suggests polymer compositions within the scope of present formula (IX).

Applicants respectfully submit that this rejection should be reconsidered and withdrawn for the same reason that the preceding three rejections should be reconsidered and withdrawn.

Claim 24 withdrawn from consideration -- Applicants' Traversal

The Examiner states that newly submitted claim 24 (as now amended) is directed to an invention that is independent or distinct from the invention originally claimed because it relates to the original claims as a process of use of the product. Per the Examiner, the inventions are distinct if the product as claimed can be used in a materially different process. This is shown for the original claims, the Examiner says, by the process of imaging used by Unruh and the process of charge carrier transport used in Teuscher.

The Examiner states that since Applicants have received an Action on the merits for the originally presented invention, this invention has been constructively elected by original presentation for prosecution on the merits. Accordingly, the Examiner says, claim 24 is withdrawn from consideration as being directed to a non-elected invention.

Applicants respectfully traverse for essentially the same reasons as stated at page 3 of the Amendment and Response filed April 9, 2001. As explained there, Applicants respectfully submit that restriction with regard to claim 24 is not warranted, appropriate or fair, because this claim merely recites a method of using the bottom anti-reflective coating material composition of claim 12 to form a resist pattern. Accordingly, Applicants respectfully request that claim 24 be rejoined and considered.

Response to Objection to Claim 19

The Examiner notes that claim 19 should not have been a choice for election because it is improperly multiply dependent in that it depends on claims 12 and 18 simultaneously.

Claim 19 is objected to as being in improper form because a multiple dependent claim should refer to other claims in the alternative only. Accordingly, claim 19 has not been further treated on the merits.

To overcome the objection to claim 19, Applicants have amended it so that it depends solely from claim 18.

In view of the above, Applicants respectfully submit that claim 19 should be treated on the merits in the next Action.

Claims 14-18 and 20 Withdrawn from Consideration -- Applicants' Response

Claims 14-18 and 20 are withdrawn from further consideration, as being drawn to a non-elected species, there allegedly being no allowable generic or linking claim. The Examiner notes that Applicants timely traversed the restriction (election) requirement.

The Examiner states that Applicants' election with traverse of species A (claim 21) as supported by specification selection of working Example 20 and request to search polymer and second component first is acknowledged. The traversal, the Examiner says, is on the grounds that claims 14-20 would cover or read on claim 21. The Examiner states that this is not found persuasive because claim 12 is the generic linking claim between species A, B and C. Only claim 21, the Examiner says, has the second specified components as elected. Since the broad

generic claim 12 is rejected, all claims without the component are no longer linked to the elected species.

The Examiner states that the requirement is still deemed proper and is therefore made final.

It appears to Applicants that the Examiner's action of withdrawing claims 14-18 and 20 from further consideration is not proper. MPEP §809.02(c), entitled Action Following Election, states that an Examiner's Action subsequent to an election of species "should include a complete action on the merits of all claims readable on the elected species." In the present case, in addition to claim 21, claims 12, 14, 15, 16, 17, 18, 24, and possibly 19 are readable on the elected species. Therefore, Applicants respectfully request the Examiner to provide an action on the merits of these claims.

Further, Applicants note with due respect that the Examiner is incorrect in stating that the election of species was with traverse.

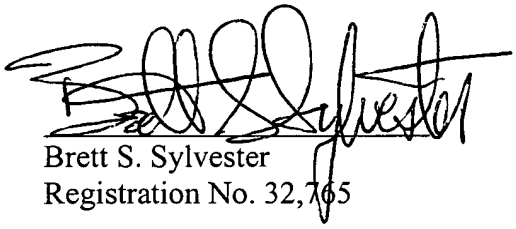
Response to Section 112 Objection

Claim 12 is objected to because in line 16 of claim 12, "toms" should be "atoms". The Examiner requires appropriate correction.

As noted above, Applicants have corrected this typographical error in claim 12.

Allowance is respectfully requested.

Respectfully submitted,



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Date: November 21, 2001

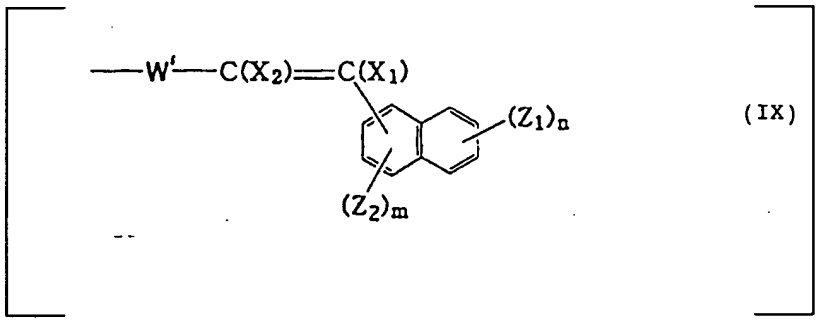
APPENDIX

VERSION WITH MARKINGS TO SHOW CHANGES MADE

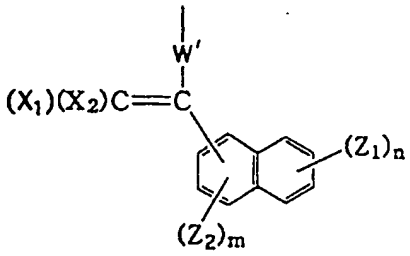
IN THE CLAIMS:

The claims are amended as follows:

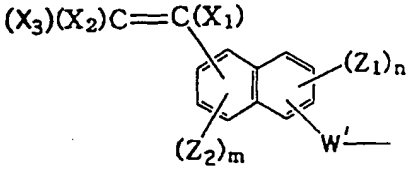
12. A bottom anti-reflective coating material composition comprising a polymer light absorbent having at least one group represented by the following formula [(IX),] (X), (XI), (XII), (XIII), (XIV) or (XV) on the side chain:



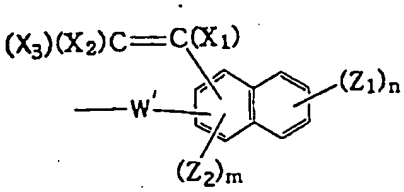
(IX)


W'
(X1)(X2)C=C
(Z1)n
(Z2)m

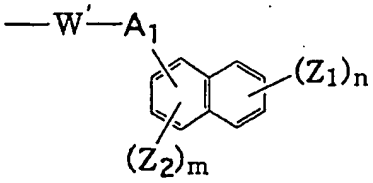
(X)


(X3)(X2)C=C(X1)
(Z1)n
(Z2)m
W'

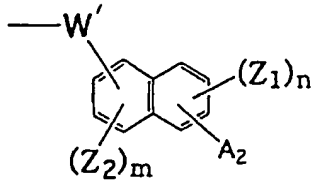
(XI)


(X3)(X2)C=C(X1)
W'
(Z1)n
(Z2)m

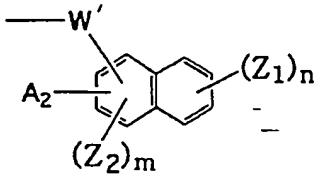
(XII)


W'
A1
(Z1)n
(Z2)m

(XIII)



(VXIV)



(XV)

wherein W' represents a divalent linking group, X_1 to X_3, which may be the same or different, each represents a hydrogen atom, a halogen atom, a cyano group or $-(X_4)_p-R$ wherein R represents an alkyl group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon [toms] atoms or an aralkyl group having from 7 to 20 carbon atoms, which may have a substituent, X_4 represents a single bond, $-CO_2-$, -CONH-, -O-, -CO-, an alkylene group having from 2 to 4 carbon atoms or $-SO_2-$, p represents an integer of from 1 to 10, Z_1 and Z_2, which may be the same or different, each represents an electron donating group, m and n represent an integer of from 0 to 2 and from 0 to 3, respectively, and when m is 2 or m and n each is 2 or 3, the Z_1 groups or the Z_2 groups may be the same or different, A_1 represents a divalent aromatic ring or heteroaromatic ring group having from 5 to 14 carbon atoms, which may have a substituent, and A_2 represents an aromatic ring or heteroaromatic ring group having from 5 to 14 carbon atoms, which may have a substituent.

19. (Amended) A bottom anti-reflective coating material composition as claimed in claim [12] 18, wherein said polymer light absorbent contains from 2 to 50 wt% of a repeating structural unit represented by formula (XXVII) of claim 18 where B_1 is a group obtained by the reaction of a group represented by $-CONHCH_2OH$, $-CONHCH_2OCH_3$, $-CH_2OCOCH_3$, $-C_6H_4(OH)CH_2OH$, $-C_6H_4(OH)CH_2OCH_3$ or $-CONHC(CH_3)_2CH_2COCH_3$, with formalin.

ATTACHMENT (1) - 09/615,708

1/4

NOV 21 2001 PATENT & TRADEMARK OFFICE

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 159 428 B1**

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **19.11.92** (51) Int. Cl.5: **G03F 7/09**

(21) Application number: **84302692.3**

(22) Date of filing: **13.04.84**

Divisional application 87113957 filed on 24.09.87.

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TC 1700

(54) Anti-reflective coating.

(43) Date of publication of application:
30.10.85 Bulletin 85/44

(45) Publication of the grant of the patent:
19.11.92 Bulletin 92/47

(84) Designated Contracting States:
DE FR GB IT NL

(56) References cited:
EP-A- 0 087 582
DE-A- 1 597 597
GB-A- 785 858
GB-A- 2 085 609
US-A- 4 362 809
US-A- 4 370 405

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JOURNAL OF APPLIED PHYSICS, vol. 55, no. 4, February 1984, pages 1110-1115, New York, USA; YI. CHINGLIN et al.: "Improvement of linewidth control with antireflective coating in optical lithography"

IBM TECHNICAL DISCLOSURE BULLETIN, vol. 13, no. 1, June 1970, page 38, New York, USA; H.A. KHOWY et al.: "Anti-interference phenomena coating"

CHEMICAL ABSTRACTS, vol. 101, no. 16, 15th October 1984, page 642, no. 140939k, Columbus, Ohio, USA; M.P.C. WATTS: "A high-sensitivity two two-layer resist process for use in high resolution optical lithography" & PROC. SPIE. INT. OPT. ENG. 1984, 469 (ADV. RESIST TECHNOLOGY) 2-10

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EP 0 159 428 B1

Description

The present invention relates to a photolithographic resist having a novel anti-reflective coating, and to processes for producing such a photolithographic resist and integrated circuit elements using such a resist, as well as to a novel composition useful in the production of such a photolithographic resist.

The miniaturizing of systems utilizing complex integrated circuits has required that increasingly complex circuitry be imprinted on chips of decreasing size. This reduction in size, or increase in volumetric capacity, has reached the point where the techniques available to the industry have been stretched to the limit of their capabilities. As it is, the yield of the most advanced integrated circuit chips produced by standard techniques is extremely low, of the order of 1%, due to attempts to put more and more capacity into a smaller and smaller volume. At the level of capacity which is being demanded by the industry today, the current photolithographic processes cannot produce a complete, workable structure more than about 1% of the time.

The problem is due to a large extent to the limitations of the photographic process used. At the microscopic level which is required, the layers of chip material, silicon, for example, are not perfectly smooth and flat. Moreover, the uneven topography is of a magnitude approximating that of the wavelength of the light which is used to form the images in the photoresistive material which is applied to the layers of the chip. The light which is used to image the photoresistive material is reflected from the substrate of the chip material, that is, the silicon wafer. This reflection, coupled with the uneven topography, causes an uneven distribution of light in the imageable material and results in a large number of artifacts being produced in the developed image. These artifacts cause a large number of rejects in any semi-conductor structure built by current techniques.

It is apparent that if artifacts can be eliminated or reduced the yield of integrated circuit chips can be increased, resulting in great efficiency and reducing the cost of producing such materials.

Recently there have been a number of attempts to reduce the artifacts caused by reflected light. U.S. Patent No. 4,102,683 discusses one such attempt. Other discussions appear in the IEEE Transactions on Electron Devices, Edition 28, No. 11 of November 1981, pages 1405 to 1410, entitled "Line Width Control and Projection Lithography Using a Multi-Layer Resist Process" by O'Toole, et al. and in "Reduction of the Standing Wave Effect in Positive Photo-Resist," Brewer, et al. in Journal of Applied Photographic Engineering, Vol. 7, No. 6, Dec. 1981, pages 184 to 186, and "Control of One-Micron Lines in Integrated Circuits," Carlson, et al., Kodak, '80 Interface, October 1980, pages 109 to 113.

We have now discovered an improved photolithographic process for integrated circuits, an improved anti-reflective material for use therein and an integrated circuit chip utilizing such material. The present process uses an anti-reflective coating that eliminates deleterious effects due to internal reflections from wafer surfaces and photoresist surfaces. The material offers better adhesion, greater light absorption, is a thinner, more uniform coating, and has a more controlled development and requires fewer process steps than those previously known. Also, it is compatible with and images with the photoresist, in the integrated circuit manufacturing process. The coating leaves less residue on the integrated circuit wafers after development.

The present invention thus consists in a photolithographic resist comprising a substrate, a photoresist and a light-absorbing imageable anti-reflective coating between said substrate and said photoresist as defined in claim 1.

The invention further consists in a process for preparing the above photolithographic resist, in which the anti-reflective coating is deposited and fixed to the substrate by depositing on the substrate a continuous layer of a solution of said polyimide resin and/or polyimide resin precursor and baking the product to remove said solvent and fix the resin to the substrate, wherein said solvent is a low surface energy solvent.

The invention still further consists in a process for making an integrated circuit element by photolithography in which a pattern is imaged in the photoresist and anti-reflective coating of the above defined resist, the anti-reflective coating imaging with the photoresist, developing and removing the developed image from the photoresist and anti-reflective coating, the imaged anti-reflective coating developing with and being removed with the photoresist, and etching a pattern defined by the imaged anti-reflective coating and photoresist into the substrate to produce said integrated circuit element.

The invention is further illustrated with reference to the accompanying drawings, in which:

Figure 1 shows a process flow for producing an integrated circuit element using an imageable anti-reflective coating; and

Figure 2 shows modified process steps using a dry etch.

The present invention uses a particular polymer, which is such as to allow the use of common organic solvents having low surface (interfacial) energy, which can produce a firmly bonded, thin and consistent coating on a wafer surface. Suitable

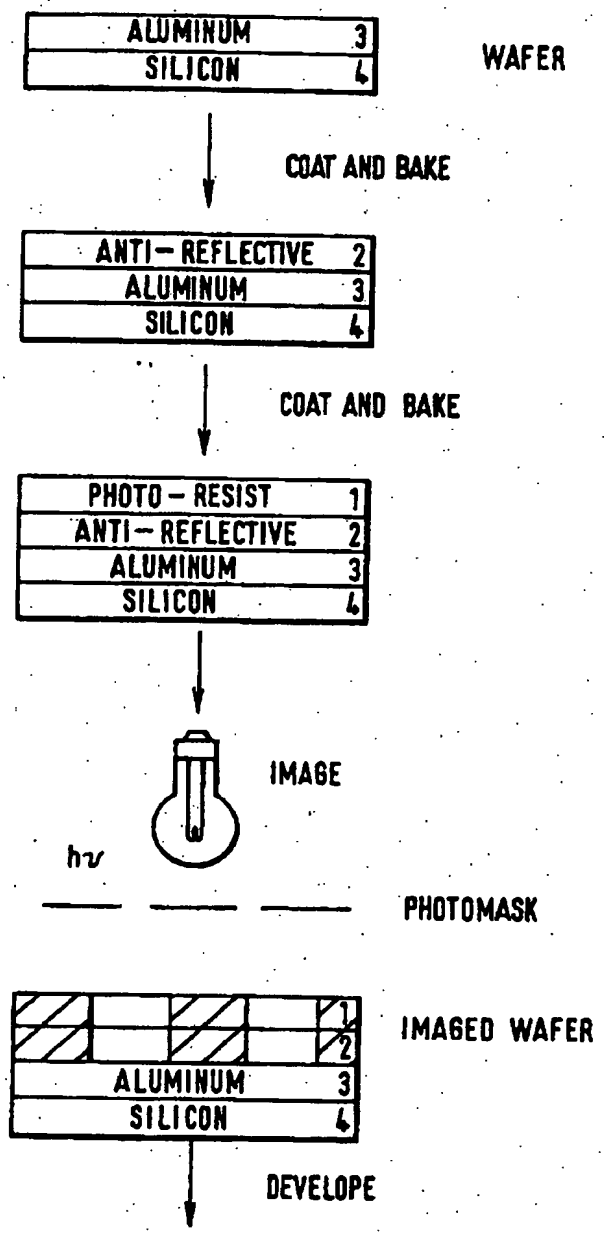

ALUMINUM 3
SILICON 4
WAFER
COAT AND BAKE
ANTI-REFLECTIVE 2
ALUMINUM 3
SILICON 4
COAT AND BAKE
PHOTO-RESIST 1
ANTI-REFLECTIVE 2
ALUMINUM 3
SILICON 4
IMAGE
hν
PHOTOMASK
1
2
ALUMINUM 3
SILICON 4
IMAGED WAFER
DEVELOPE

FIG.1A.

FIG.1B.

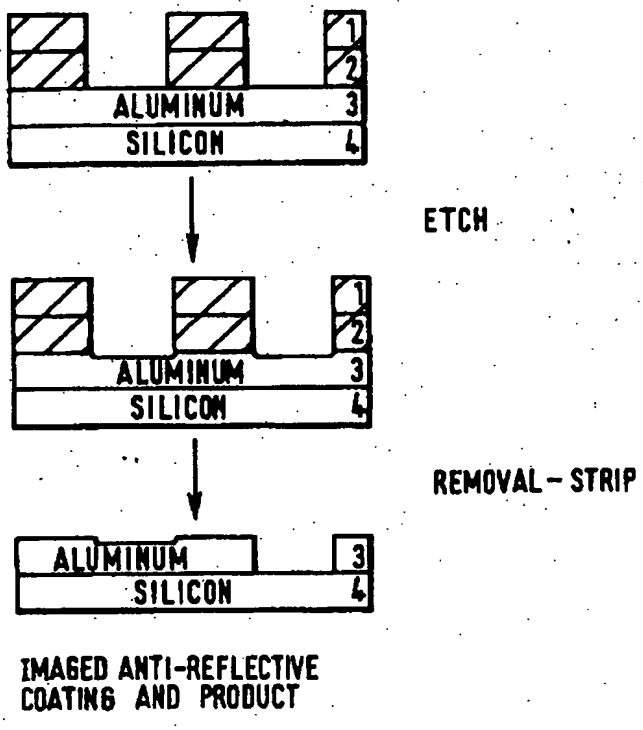
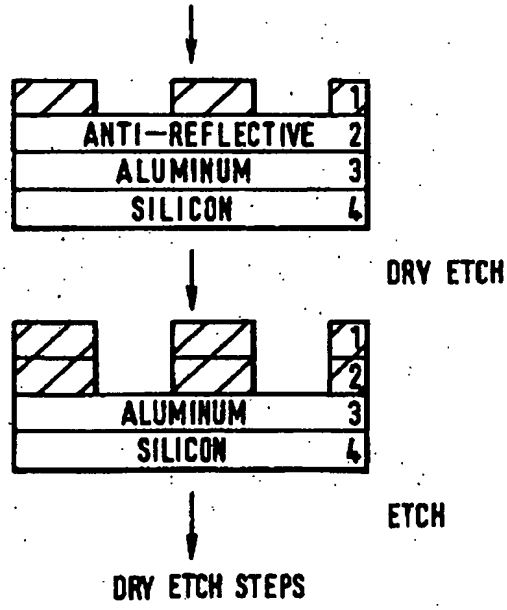

1
2
ALUMINUM
3
SILICON
4
ETCH
1
2
ALUMINUM
3
SILICON
4
REMOVAL - STRIP
ALUMINUM
3
SILICON
4
IMAGED ANTI-REFLECTIVE COATING AND PRODUCT

FIG.2.


1
ANTI-REFLECTIVE
2
ALUMINUM
3
SILICON
4
DRY ETCH
1
2
ALUMINUM
3
SILICON
4
ETCH
DRY ETCH STEPS

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ATTACHMENT ② - 09/615,708

PHOTOREACTIVE POLYMERS

THE SCIENCE AND TECHNOLOGY OF RESISTS

Arnost Reiser
Institute of Imaging Sciences
Polytechnic University
Brooklyn, New York

WILEY
A WILEY - INTERSCIENCE PUBLICATION
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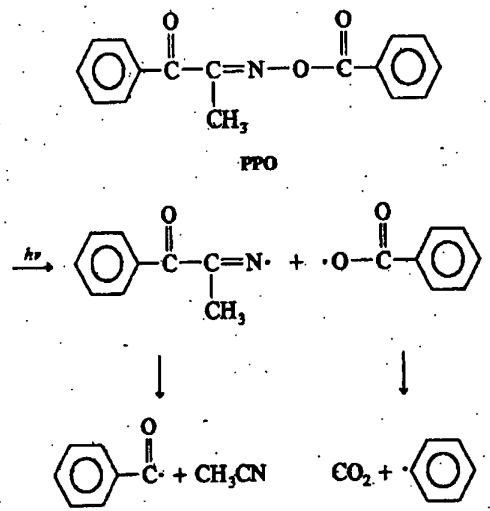
Ketoxime Esters of Benzoin. The idea of secondary fragmentation, which counteracts cage recombination and leads eventually to small, highly reactive radicals, is taken one step further in the ketoxime esters first introduced by Delzenne and co-workers [29]. For example, in the photolysis of 1-phenyl-1,2-propanedione-2-*O*-benzoyloxime (PPO), *two* volatile fragments are eliminated after primary scission of the N—O bond.



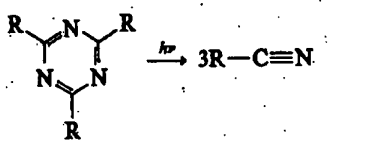
PPO

(19)

The radical yield of PPO is high ($\phi_i = 0.9$) and the phenyl radical, the final product of fragmentation, is an aggressive initiating species. In the polymerization of methyl methacrylate, the overall initiating efficiencies of some of these initiators are in the order

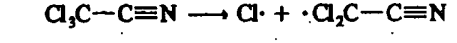
PPO > DEAP > benzoin ethers

Triazines. Another system where multiple fragmentation is brought about by α scission are the symmetrical triazines, which on excitation dissociate into three substituted nitriles [30].



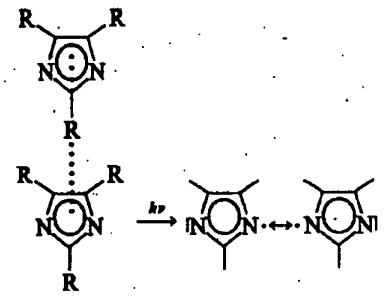
(20)

Here the primary photoproducts are not radicals, but they dissociate into radicals in a secondary thermal step.



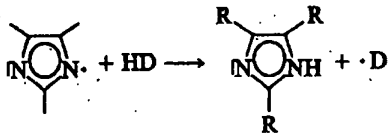
(21)

Biimidazoles. A novel type of initiator based on the idea of incorporating a particularly weak bond into a molecule are the heavily substituted aryl-biimidazoles [31, 32].



(22)

They are obtained from the corresponding imidazoles by treatment with mild oxidants. The two moieties of the biimidazole are held together by a weak bond between nitrogen atoms and dissociate on excitation with almost unit efficiency into two imidazolyl radicals that are highly stabilized by resonance and have consequently long radical lifetimes. They do not initiate polymerization, but they will react with hydrogen donors, for example with tertiary amines, and produce in this way active radicals capable of initiating polymerization.



(23)

Radicals Generated by Hydrogen Abstraction

Hydrogen abstraction by the excited triplet states of ketones is one of the classic reactions of organic photochemistry. Irradiation of benzophenone, for example, in the hydrogen donor solvent isopropanol leads to the following

processes:

$$Ph_2CO \xrightarrow{h\nu} {}^1Ph_2CO^* \longrightarrow {}^3Ph_2CO^*$$

$$^3Ph_2CO^* + H-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-OH \longrightarrow Ph_2\dot{C}O-H + \cdot\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-OH \qquad (24)$$

mixed dimers

$$Ph_2\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}-\underset{\displaystyle OH}{\overset{\displaystyle |}{CPh_2}} \qquad HO-\underset{\displaystyle H_3C\ CH_3}{\overset{\displaystyle H_3C\ CH_3}{\underset{|}{\overset{|}{C}}}}-\underset{|}{C}-OH$$

In the absence of any other reactive species the radicals formed by hydrogen abstraction combine into dimers, but in the presence of a reactive monomer they initiate chain polymerization. The species that absorbs radiation and is promoted to an excited state is termed the initiator, the hydrogen donor is the coinitiator.

The triplet excited states of common (aromatic) ketones are known to have $n\pi^*$ configurations, that is, they are formed by promoting an electron from a nonbonding n orbital on oxygen into an antibonding π^* orbital that is delocalized over the aromatic π system. Charge delocalization produces a partial positive charge on oxygen that may interact with the electron rich C—H bond and lower the energy of the transition state for hydrogen abstraction.

$$\left[Ph_2C=\overset{\delta-}{O}\cdots\overset{\delta+}{H}-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-OH\right]^*$$

Ketones with $\pi\pi^*$ configurations in the triplet state are less polar and hence less reactive. While $n\pi^*$ triplets abstract hydrogen from alcohols and even from tertiary C—H bonds of hydrocarbons, $\pi\pi^*$ triplets are slow to react with alcohols and will only react efficiently with tertiary amines, the strongest hydrogen donors [33].

In general, the success of the hydrogen abstraction step

$$R_2CO^* + H-D \longrightarrow R_2\dot{C}O-H + \cdot D \qquad (25)$$

depends on the bond dissociation energies involved and on polar effects in the transition state [34]. Rate constants for the reaction of benzophenone triplets with a range of hydrogen donors are listed in Table 4-2.

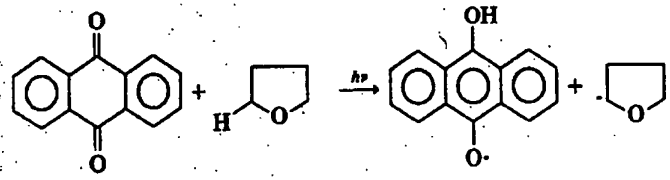
TABLE 4-2 Rate Constants for the Reaction of Benzophenone Triplets with Various Hydrogen Donors [12]

Donor	k_q
Benzene	10^4
Cyclohexane	4×10^4
Methanol	3×10^5
Ethanol	6×10^5
Isopropanol	1×10^6
THF[a]	4.5×10^6
n-Nonylmercaptan	1×10^7
Thiophenol	3×10^8
Triethylamine	2×10^9
(Oxygen)	(2×10^9)
Phenyl dimethylamine	3×10^9

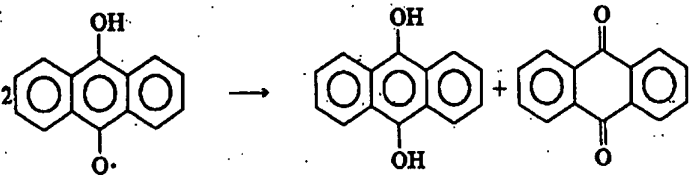
[a] Tetrahydrofuran is abbreviated as THF.

Practical Initiator Systems Based on H Abstraction [35]

Anthraquinone and Tetrahydrofuran



Anthraquinone THF (26)



Here, the tetrahydrofuryl radical is the principal initiating species [36]. For better solubility, 2-ethylanthraquinone or 2-*tert*-butylanthraquinone are recommended, or in aqueous systems, anthraquinone sulfonate.

Benzophenone and Tertiary Amines. Benzophenone and tertiary alcohols had been used for some time as initiators when Sander et al. [37] discovered the dramatic enhancement of initiating efficiency brought about in these systems by small additions of tertiary amines. It was found that the effect was caused not only by the good hydrogen donor properties of the alkyl groups in the α position to nitrogen, but also by the ability of the amines to act as electron donors and form *exciplexes* (excited complexes, see Chapter 3) with the triplet

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Library of Congress Cataloging in Publication Data:

Reiser, Arnost.
Photoreactive polymers: the science and technology of resists/
Arnost Reiser.
p. cm.
"A Wiley-Interscience publication."
Bibliography: p.
Includes index.
ISBN 0-471-85550-2
1. Polymers and polymerization. 2. Imaging systems.
3. Photoresists. I. Title.
QD382.P45R45 1988
621.36'7—dc19 88-26092
CIP

Printed in the United States of America

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Organic Photochemistry. VII. The Photosensitized and Thermal Cycloaddition Reactions of 1,3-Butadiene, Isoprene, and Cyclopentadiene to α-Acetoxyacrylonitrile. 1,2 *vs.* 1,4 Addition as a Function of Sensitizer Triplet Energy in Cross-Addition Reactions[1,2]

Wendell L. Dilling, Roger D. Kroening, and J. C. Little

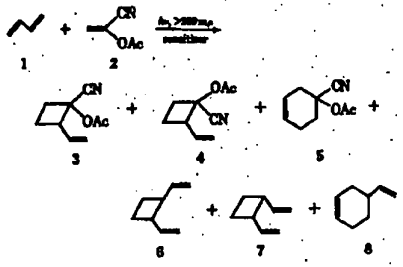
Contribution from the Edgar C. Britton Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640.
Received June 9, 1969

Abstract: Ultraviolet irradiation of 1,3-butadiene and α-acetoxyacrylonitrile in the presence of triplet sensitizers gave *cis*- and *trans*-1-cyano-2-vinylcyclobutyl acetate, 1-cyano-3-cyclohexen-1-yl acetate, *cis*- and *trans*-1,2-divinylcyclobutane, and 4-vinylcyclohexene in high yield at low conversions (*ca.* 10–20%). At higher conversions increasing amounts of a copolymer were formed. The product distribution as a function of the energy of the lowest triplet state of the sensitizer was found in general to parallel the product distribution in the dimerization of butadiene and isoprene studied by Hammond and coworkers. Possible reasons for the variation which was observed are discussed. Side reactions such as oxetane formation and pinacol reduction with the ketonic sensitizers were examined. α-Acetoxyacrylonitrile underwent a rather inefficient photosensitized dimerization. The unsensitized photoaddition of 1,3-butadiene and α-acetoxyacrylonitrile gave cycloaddition products in a very inefficient reaction. The photosensitized cycloaddition of isoprene to α-acetoxyacrylonitrile gave a mixture of methyl-substituted 1-cyano-1-acetoxy-2-vinylcyclobutanes and 4-cyano-4-acetoxycyclohexenes in addition to cyclodimers of isoprene. The distribution of products was also dependent on the triplet energy of the sensitizer in much the same manner as for butadiene. The thermal cycloaddition reaction of isoprene with α-acetoxyacrylonitrile gave 95% cyclohexene adducts and 5% cyclobutane adducts. The photosensitized cycloaddition of cyclopentadiene to α-acetoxyacrylonitrile gave a mixture of cyanoacetoxybicyclo[2.2.1]- and -[3.2.0]heptenes in addition to cyclodimers of cyclopentadiene. The distribution of products was not dependent on the sensitizer. The head-to-head structure of the 1,2-addition product was established by an alternate synthesis. The thermal cycloaddition reaction of cyclopentadiene with α-acetoxyacrylonitrile gave only norbornene adducts. A linear free energy relationship for predicting *endo*–*exo* ratios in thermal cycloadditions of 1,1-disubstituted ethylenes is proposed.

The photochemical cycloaddition of conjugated dienes to other olefins to give cyclobutane derivatives and other cyclic products is a well-established type of reaction and has considerable synthetic utility.[1] We have examined in some detail the photosensitized cross-additions of 1,3-butadiene (1), isoprene (18), and cyclopentadiene (32) to α-acetoxyacrylonitrile (2). The photocycloaddition reaction of the olefins 1 and 2 was of particular interest in view of the fact that these two olefins undergo simultaneous 1,2- and 1,4-thermal cycloadditions.[3] Also, no photocycloadditions of α,β-unsaturated nitriles to dienes had been reported. It was hoped that a study of the photoaddition might aid in an understanding of the mechanism of the thermal reaction. The thermal cycloaddition reactions of the dienes 18 and 32 with 2 were also examined.

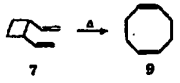
Results

1,3-Butadiene. Irradiation of an equimolar mixture of the diene 1 and α,β-unsaturated nitrile 2 with a triplet sensitizer gave a mixture of three cross-adducts 3–5 and three dimers of butadiene 6–8. In addition to these six products, a few minor components were formed in



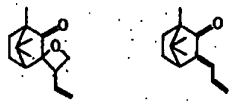
some cases, and at higher conversions (>~20% depending on the sensitizer) a 1.3:1 copolymer of 1 and 2 was formed.

The cyclobutane cross-adducts 3 and 4 were identified by nmr spectral comparisons of a mixture of the two collected by preparative gc with an authentic mixture prepared by the thermal reaction of 1 and 2.[3] The two cyclobutanes 3 and 4 were not separated, but the presence of both isomers was established by the observation of two acetyl methyl peaks at −2.07 and −2.05 ppm in the nmr spectrum of the isolated mixture. The cyclohexene cross-adduct 5 had retention times identical with that of authentic material[3] on three different gc columns as did the isomeric cyclobutanes 3 and 4. The three dimers of butadiene 6–8 were prepared by the method of Hammond and coworkers,[4] and identified by comparison of the nmr and infrared spectra with authentic materials or data in the literature. The *cis*-divinylcyclobutane 7 was analyzed and isolated as the thermal rearrangement product, 1,5-cyclooctadiene (9).[4c,5] This thermal isomerization presumably occurs



in the injection port of the gas chromatograph (temperature *ca.* 220°). We have not established that the divinyl compound 7 is the photoproduct in our reaction, but assume that it is based on Hammond's work.[4]

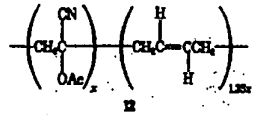
In most cases the sensitizers were recovered unchanged at the end of the reaction. One notable exception was camphorquinone. In addition to undergoing energy transfer this diketone reacted with the diene 1 to give an oxetane or oxetanes in both the presence and absence of the unsaturated nitrile 2. The evidence indicated that the structure of the oxetane was 10 and/or closely related isomers. The gas chromatogram of the reaction mixtures containing 10 indicated



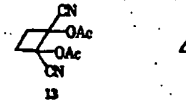
that several isomers may have been present. The spectral data obtained from the oxetane fraction isolated by preparative gc were in accord with structure 10 or a closely related isomer. The mass spectrum showed a molecular ion peak, *m/e* 220, and principal peaks at *m/e* 192 ($M^+ - CO$ or C_2H_4), 166 ($M^+ - C_4H_6$), 138 ($M^+ - C_4H_6$ and CO or C_2H_4), 123 ($M^+ - C_4H_6$ and C_3H_7 or C_3H_5O), and 109 ($M^+ - C_4H_6$ and C_3H_8 or C_3H_6O). The infrared spectrum showed the presence of a vinyl group (3090 cm⁻¹, CH stretch; 1860, CH_2 wag overtone; 1650, C=C stretch; 1405, CH in plane deformation; 994, –CH=CH_2 twist; 923, CH_2 wag) and a five-membered ring ketone, 1750 cm⁻¹. Evidence for the *gem*-dimethyl group, doublet ~1380 cm⁻¹, and the oxetane ring, ~980 cm⁻¹, was also observed. In another preparation of the oxetanes, the product was pyrolyzed in the injection port of the gas chromatograph (*ca.* 220°). The product(s) collected were assigned the structure 11 or closely related isomers which would result from the loss of formaldehyde from the oxetane 10.[6] The mass spectrum showed a molecular ion peak, *m/e* 190, and ion peaks for the losses of CH_3, *m/e* 175; CO or C_2H_4, *m/e* 162; C_3H_7 or CH_3CO, *m/e* 147; C_4H_9 or C_3H_5CO, 133; and C_5H_{10} or C_3H_6CO, *m/e* 120. The infrared spectrum indicated the presence of a vinyl group, and, moreover, a conjugated diene by the appearance of two C=C stretching absorption bands at 1650 and 1605 cm⁻¹. The carbonyl frequency of 1730 cm⁻¹ was appropriate for this structure, and the pair of bands for the *gem*-dimethyl group was apparent. The nmr spectrum of 11 indicated the material was not pure dienone 11 but was entirely consistent with this as a major component. Multiplets appeared at −6.75 to −5.11 ppm for the vinylic protons, at −2.96 to −1.25 for the protons on secondary and tertiary carbon atoms, and at −1.25 to −0.68 for the methyl groups. The appearance of at least six methyl peaks indicated that more than one isomer was present since 11 should give only three unsplit methyl peaks. A doublet appeared at −2.83 ppm (J = 4.3 cps), probably due to the bridgehead proton. The absence of absorption in the −4.0 to −5.0 ppm region ruled out the presence of any oxetane.[6,7]

Material balances were determined for the reactions employing acetophenone, benzophenone, biacetyl, and benzil as sensitizers using *p*-bromotoluene as an internal standard (added at the end of the irradiation to avoid possible complications due to sensitization or quenching) for the gc analysis. In the acetophenone- and benzophenone-sensitized reactions (11 and 17% conversions of 1, respectively), the butadiene was essentially all accounted for in the dimers and cross-adducts while in the biacetyl- and benzil-sensitized reactions (44 and 27% conversions of 1, respectively) 20–40% of the diene 1 which disappeared was not accounted for. This material is undoubtedly in the polymer which was formed.

The polymer obtained in the benzophenone-sensitized reaction was insoluble in common solvents and had a composition of 1.0 part of nitrile 2 to 1.35 parts of diene 1 based on the elemental analysis. Mass spectral analysis of the copolymer at 150–300° showed the presence of 1–5% of benzophenone. The latter may have been incorporated into the polymer, and observed mass spectrometrically due to thermal degradation of the polymer, or the benzophenone may have been occluded in the polymer network. The infrared spectrum of the polymer showed bands for vinylic and aliphatic C–H stretch, 3052 (sh), 2940, 2860 cm⁻¹; C≡N stretch, ~2300; C=O stretch, 1755; C=C stretch, ~1675. A fairly intense band at 973 cm⁻¹ was indicative of a *trans*-vinylene group.[8] A likely partial structure for this copolymer is 12.



Irradiation of the nitrile 2 in the presence of acetophenone gave a very slow (compared with cross-addition) conversion to two dimeric products, tentatively assigned structures 13 and 14 on the basis of spectral



and chromatographic data. The assignment of stereochemistry to the isomers 13 and 14 is tentative. This

(1) Part VI: W. L. Dilling, *Chem. Rev.*, 69, 845 (1969).
(2) Preliminary accounts of this work have been reported in parts II–V of this series: (a) W. L. Dilling and J. C. Little, *J. Am. Chem. Soc.*, 89, 2741 (1967); (b) W. L. Dilling, *Ibid.*, 89, 2742 (1967); (c) W. L. Dilling and R. D. Kroening, *Tetrahedron Lett.*, 5101 (1968); (d) W. L. Dilling and R. D. Kroening, *Ibid.*, 5601 (1968).
(3) J. C. Little, *J. Am. Chem. Soc.*, 87, 4020 (1965).

(4) (a) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, 83, 4674 (1961); (b) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, 28, 3297 (1963); (c) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 3406 (1965).
(5) E. Vogel, *Ann.*, 615, 1 (1958).
(6) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).
(7) J. K. Bradshaw, *J. Org. Chem.*, 31, 237 (1966).
(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p 54.

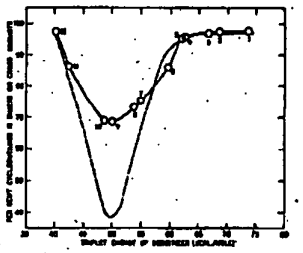


Figure 1. Butadiene-α-acetoxyacrylonitrile cross-adduct composition vs. triplet energy of sensitizer (solid line). Butadiene dimer composition (dashed line, Liu, Turro, and Hammond's data[4c]).

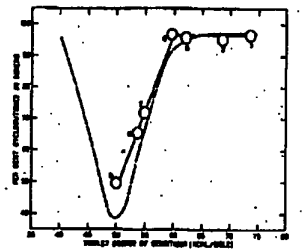


Figure 2. Butadiene dimer composition vs. triplet energy of sensitizer (solid line, this work; dashed line, Liu, Turro, and Hammond's data[4c]).

assignment is based on the relative chemical shifts of the acetoxy methyl protons, −2.23 ppm *cis* to cyano, −2.20 ppm *trans* to cyano. The above stereochemical assignment is in agreement with the expectation that the *trans* isomer 13 would predominate in the photodimerization reaction. The ratio of 13 to 14 was 57:43, respectively. The head-to-head nature of these dimers has not been established, but is assumed to be such by analogy to the photosensitized dimerization of acrylonitrile.[9] No more than trace amounts of these dimers 13 and 14 were formed in the cross-addition reactions.

The distribution of the cross-adducts and diene dimers is given in Table I. These data are plotted in Figures 1 and 2 for the cross-adducts and dimers, respectively. For comparison, the data of Hammond and coworkers[4c] are also plotted on each graph (dashed line).

Table I. Composition of Products from Photosensitized Cross-Addition of Butadiene and α-Acetoxyacrylonitrile

Sensitizer no.	Sensitizer[a]	E_T,[b]	Distribution of cross-adducts and dimers, % 3 + 4[d]	5	6	7	8
1	Acetophenone	73.6	34	0.7	56	7	2
2	Benzophenone	68.5	33	0.9	54	10	3
3	Triphenylene[e]	66.6	30	0.9	69	*f*	*g*
4	Anthraquinone[e,h]	62.4	60	3	31	6	*g*
5	Flavone	62.0	32	1.6	52	12	3
6	β-Naphthyl phenyl ketone	59.6	41	7	47	4	2
7	Biacetyl	54.9	38	12	28	7	14
8	Benzil	53.7	34	12	30	5	18
9	Camphorquinone	50.0	28	12	23	7	29
10	Pyrene[e]	48.7	38	17	34	11	*g*
11	Anthracene[e]	42.5	41	6	45	8	*g*
12	9,10-Dibromoanthracene[e]	40.2	45	1	44	10	*g*

[a] Sensitizer (1.0 mmole) in 5.0 mmoles of 1 and 5.0 mmoles of 2 irradiated through a Pyrex filter at ca. 30°. [b] Lowest triplet energy level in kilocalories per mole. See ref 4c and 10. [c] Determined by gas chromatography with each component corrected for thermal conductivity variation in detector. [d] The *cis* and *trans* isomers were not separated. [e] Saturated solution of sensitizer in an equimolar mixture of 1 and 2. [f] Not determined due to low overall conversion. [g] Not determined due to interference by large excess of 2 and presence of small amount of 8 in the starting diene 1. [h] A larger amount of polymer was formed in this reaction.

(9) (a) J. Runge and R. Kacha, British Patent 1,058,230 (1967); *Chem. Abstr.*, 67, 73215 (1967); (b) S. Hosaka and S. Wakamatsu, *Tetrahedron Lett.*, 219 (1968); (c) R. S. H. Liu and D. M. Gale, *J. Am. Chem. Soc.*, 90, 1897 (1968); (d) J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 5901 (1968); see also (e) M. Herberhold and G. S. Hammond, *Ber. Bunsenges. Phys. Chem.*, 72, 309 (1968).

and coworkers[4c] are also plotted on each graph (dashed line).

The relative amounts of the *cis* and *trans* isomers 3 and 4 were not determined except in the benzophenone-sensitized reaction. In this case two isomers were present in nearly equal concentrations, with the isomer having the lower field acetyl methyl resonance in the nmr predominating to a slight extent.

The relative yields with sensitizers numbered 3, 4, 10–12 were considerably lower than the others shown in Table I. An attempt to use naphthalene, E_T = 60.9 kcal/mole,[10] as a sensitizer in this cross-addition was unsuccessful; no reaction was observed.[11]

The product distribution at various stages of conversion for five sensitizers is shown in Table II. It will be noted that the relative amount of cyclobutane cross-adducts 3 and 4 in the total cross-adducts 3–5 did not vary appreciably. However the relative amounts of total cross-adducts 3–5 to total dimers 6–8 did vary at higher conversions.

The effect of changing the ratio of the diene 1 and the olefin 2 was determined for one sensitizer, acetophenone. The product distribution shown in Table III indicates, as expected, that increasing the amount of 2 increased the amount of cross-adducts 3–5 relative to the dimers 6–8.

A brief study of solvent effects on this reaction indicated that the major effect was to decrease greatly the efficiency of the addition. Irradiation of 1 and 2 with acetophenone in ether solution for 2 days gave only a 3–4% conversion of the nitrile 2 to the cross-adducts, primarily the cyclobutanes 3 and 4. Irradiation of the two olefins in acetonitrile and dimethyl sulfoxide solutions with acetophenone as the sensitizer gave the results shown in Table IV. The isomer distributions for the latter two reactions were not appreciably different from that obtained when no solvent was used. In an attempted large-scale run using benzophenone as the sensitizer in ether solution, irradiation for 5 days gave a 5–10% conversion to the cross-adducts, primarily 3 and 4. Further irradiation failed to increase the cross-adduct concentration, and gave only additional polymer.

The cross-adducts 3–5 were relatively stable under the reaction conditions (no solvent) using benzophenone as the sensitizer. No indication of increased polymeriza-

(10) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 4537 (1964).

(11) Similar results have been observed by L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, 16, 125 (1968).

Table II. Dependence of Product Distribution on Extent of Conversion

Sensitizer no.	Sensitizer[a]	Time,[b]	Distribution of cross-adducts and dimers, % 3 + 4	5	6	7	8	Cyclobutanes in cross-adducts, %	Cyclobutanes in dimers, %	Conversion, %	Sensitizer converted, %
1	Acetophenone	1	34	0.7	56	7	2	98	97	11 (1)[c]	
		4[d]	35	*e*	60	5	*f*			>47 (1)	
		24[g]	52	*e*	38	10	*f*				
2	Benzophenone	1	33	0.9	54	10	3	98	95	17 (1)	
		4[d]	31	*e*	59	10	*f*			>58 (1)	
		24[g]	96	*e*	2	2	*f*				
3	Triphenylene[h]	2	30	0.9	69	*i*	*f*	97		0.5 (2)[j]	
		4[g]	76	3	21	*i*	*f*	96			
7	Biacetyl	1	38	12	28	7	14	76	72	44 (1)[j]	
		4[g]	36	11	34	8	*f*	77			
9	Camphorquinone	0.25	26	10	29	4	31	72[k]	52	1 (2)	5
		0.50	27	12	28	6	27	69	56	4 (2)	19
		1.0	28	12	23	7	29	69	50	9 (2)	29

[a] Sensitizer (1.0 mmole) in 5.0 mmoles of 1 and 5.0 mmoles of 2. [b] Irradiation time in hours, Pyrex filter, ca. 30°. [c] Per cent of diene 1 converted to cross-adducts, dimers, or polymer. [d] A small amount of polymer was formed in the reaction. [e] Not determined due to lower sensitivity in analytical gc method. [f] Not determined due to interference by the presence of 2 and presence of a small amount of 8 in the starting diene 1. [g] A large amount of polymer was formed in the reaction. [h] Saturated solution of sensitizer in equimolar mixture of 1 and 2. [i] Not determined due to low overall conversion. [j] Per cent of olefin 2 converted to cross-adducts. [k] Least accurate of three runs due to low conversion.

Table III. Effect of Monomer Ratio on Product Distribution [Acetophenone (15) Sensitized][a]

Ratio of monomers 2/1	Distribution of cross-adducts and dimers, % 3 + 4	5	6	7	8	1 converted, %
0.1[b]	5	*c*	83	9	~3	6
1.0[d]	34	0.7	56	7	2	11
5[e]	88	1	11	*c*	*c*	12

[a] Irradiated for 1 hr through Pyrex filter at ca. 30°. [b] Molar ratio of reactants: 9.52:1.00:0.95 1:2:15. [c] Concentration too low to determine. [d] Molar ratio of reactants: 1.05:1.00:0.20 1:2:18. [e] Molar ratio of reactants: 1.00:8.17:0.80 1:2:15.

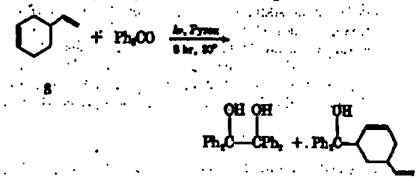
Table IV. Solvent Effect on Photoaddition of Butadiene and α-Acetoxyacrylonitrile [Acetophenone (15) Sensitized][a]

Solvent[b]	Distribution of cross-adducts and dimers, % 3–5	6–8	1 converted,[c] %
None	35	65	11
MeCN	37	63	1.7
Me_2SO	34	66	2.2

[a] Irradiated through Pyrex for 1 hr at ca. 30°. [b] 5 mmoles of 1, 5 mmoles of 2, and 1 mmole of 15 in 10 ml of solvent. [c] Determined by using *p*-bromotoluene as an internal standard.

tion was noted when an excess of these components was added before the irradiation. In contrast irradiation of diene 1, olefin 2, and benzophenone in the presence of 10 mole % (based on 1 or 2) of vinylcyclohexene (8) markedly increased the rate of polymer formation although the olefin 8 was largely recovered. Cyclohexene caused only a slight increase in the amount of polymerization, but a new unidentified material was produced in quantities greater than any of the products 3–8.

Vinylcyclohexene (8) and benzophenone when irradiated through Pyrex gave a mixture of products, the major of which were benzopinacol (16) and a material tentatively identified as the 1:1 adduct 17, or a closely related isomer.[12] The structure of the adduct 17, which was not isolated in a pure state, was based on spectral evidence. The mass spectrum showed a molecular ion peak at *m/e* 290 and an intense peak at *m/e* 272 ($M^+ - H_2O$). The infrared spectrum confirmed



the presence of a hydroxyl group, ν 3580, ~3500 cm⁻¹, and also exhibited bands consistent with the remainder of the structure: 3090 (vinyl CH stretch), 3070, 3035 (aromatic CH stretch), 2930 (aliphatic CH stretch), 1650, 1610, 1590 (vinyl and aromatic C=C stretch), 1000, 920 (–CH=CH_2 twist and wag), and 700 (phenyl CH out-of-plane deformation). The nmr spectrum showed the material to be a mixture but the appearance of signals at −7.8 to −6.9 ppm (11.1 H) for aromatic protons, −6.1 to −4.6 (3.4 H) for vinylic protons, and −3.8 to −0.9 (7.4 H) for protons on saturated carbon was consistent with the presence of 17. This side reaction probably did not effect the isomer distribution shown in Table I since the conversion was rather low.

Addition of 2 mole % (based on 1 or 2) of a known free-radical polymerization inhibitor, 4,6-dinitro-*o*-cresol, decreased markedly the rate of polymerization, but also greatly decreased the rate of cycloaddition. Using benzophenone as the sensitizer, this reaction gave only a 2% conversion of the nitrile 2 to the cross-adducts 3–5 in 4 hr in contrast to the >58% (Table II) conversion of diene 1 in the absence of the inhibitor.

Control reactions established the absence of any cycloaddition or polymerization reactions on irradiation of 1 and 2 through Pyrex in the absence of a sensitizer.

Direct irradiation of an equimolar mixture of the olefins 1 and 2 contained in quartz tubes with either a me-

(12) Bradshaw[9e] has reported a similar reaction with cyclohexene.